THE CATIONS KrF^+, XeF_3^+, $XeOF_3^+$ AND $XeOF_5^+$
AND OXIDIZING PROPERTIES OF KrF^+

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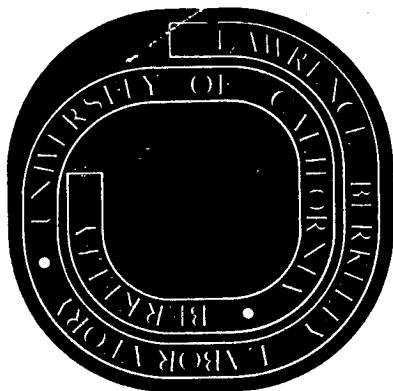
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Summary - The $XeOF_5^+$ ion (prepared by exploiting KrF^+ as an oxidizer) is related to, but distinguishable from $XeOF_3^+$; the latter is in turn related to XeF_3^+, the geometry of which has been established by X-ray crystallography.

In earlier communications[1] we showed that the adduct[2] $KrF_2 \cdot 2SbF_5$ was the salt $KrF^+Sb_2F_{11}^-$. The stretching frequency $\nu(Kr-F^+) = 626$ cm^{-1} is in excellent agreement with Schaefer's theoretical prediction[3] of 620 cm^{-1}.

In accord with the anticipated[4] high value of the electron affinity of KrF^+, the cation has proved to be an extraordinary oxidizer. We have previously shown[1] that it oxidizes IF_5 to IF_6^+ and have now carried out the oxidation of $XeOF_4$ to $XeOF_5^+$ ($XeOF_4 + KrF^+ \rightarrow XeOF_5^+ + Kr$). Since the syntheses, which involve addition of $XeOF_4$ to $KrF^+Sb_2F_{11}^-$ (~ -10), have been executed in quartz apparatus, there has always been some contamination from O_2^+ salts, but the best preparations have yielded no $XeOF_3^+$ salts. Raman data for $XeOF_5^+$ (compared with data for IOF_5 and its Xe relatives in Figure 1) show a pattern of lines consistent with an IOF_5-like species, but the Xe-F and Xe-O stretching frequencies are lower than for IOF_5. As may be seen from Figure 1, this is akin to the situation in XeF_5^+ salts, where $\nu_{symm}(Xe-F)$ tends to be somewhat lower than $\nu_{symm}(I-F)$ in IF_5.

As part of our study[5,6,7] of the fluoride ion donor abilities of the xenon fluorides and oxyfluorides, we have also investigated the systems $XeOF_4/SbF_5$ and XeF_4/SbF_5: moreover, unambiguous identification of the $XeOF_5^+$ ion demanded a full characterization of the former system. A combination of X-ray crystallographic and Raman spectroscopic data has established that XeF_3^+ is the only cation present in the XeF_4/SbF_5 system; Raman spectroscopic evidence indicates that the $XeOF_3^+$ cation is the only one present in the $XeOF_4/SbF_5$ system. Since the onset of our studies Gillespie and his coworkers have given vibrational and ^{19}F nmr spectroscopic evidence for both XeF_3^+ (Ref. 8) and $XeOF_3^+$ (Ref. 9).

Our studies have shown that in the XeF_4/SbF_5 system there are two compounds, $XeF_3^+SbF_6^-$ and $XeF_3^+Sb_2F_{11}^-$: efforts to make $Xe_2F_7^+SbF_6^-$ have failed. Both salts are pale yellow-green solids. $XeF_3^+SbF_6^-$ (m.p. 109-113°) is dimorphic, with a transition temperature of ~90°; the low temperature form is monoclinic with $\underline{a}$ = 5.50, $\underline{b}$ = 15.50, $\underline{c}$ = 8.95 (all ± 0.01 Å), $\underline{\beta}$ = 102.9 ± 0.3°, $\underline{V}$ = 743.3 Å^3, $\underline{z}$ = 4, $\underline{D}_c$ = 3.81 g cm^{-3}. $XeF_3^+Sb_2F_{11}^-$ (m.p. 81-83°) is triclinic with $\underline{a}$ = 8.237(5), $\underline{b}$ = 9.984(20), $\underline{c}$ = 8.004(5), $\underline{\alpha}$ = 72.54(5), $\underline{\beta}$ = 112.59(7), $\underline{\gamma}$ = 117.05(21)°, $\underline{V}$ = 534.9 Å^3, $\underline{z}$ = 2, $\underline{D}_c$ = 3.98 g cm^{-3}. The structure of the latter has been successfully refined in space group $P\overline{1}$ using three-dimensional graphite-monochromatized $\underline{MoK}_\alpha$ X-ray data. With anisotropic temperature factors for all atoms, a final conventional $\underline{R}$ factor of 0.035 for 1823 independent reflections for which $\underline{I} \geq 3\underline{\sigma}(\underline{I})$ has been obtained. The crystal structure is built up from the structural units, $XeF_3^+Sb_2F_{11}^-$, shown in Figure 2. The $\underline{T}$ shaped cation is planar and lies in the same plane as a fourth fluorine atom, which makes a close contact of 2.50 Å

to the xenon atom. This interaction of the cation and the anion is consistent with a distorted trigonal bipyramidal configuration of two axial F ligands, one equatorial F ligand and two sterically active, equatorial, non-bonding valence-electron pairs about the Xe atom. Such a cation should have a maximum polarizing effect normal to the tri-angular faces containing the two non-bonding pairs. As in the electroni-cally related molecules ClF_3 (Ref. 10) and BrF_3 (Ref. 11) the axial bonds in XeF_3^+ (1.88 and 1.89 Å) are longer than the equatorial (1.83 Å). This is consistent with designation of the latter as an electron-pair bond and the former as three-center four-electron bonds[4,12].

In the $XeOF_4/SbF_5$ system, Selig had previously established[13] the compound $XeOF_4 \cdot 2SbF_5$, but structural information was lacking until the recent report by Gillespie and his coworkers[9]. In our studies, two compounds have been isolated (1:1, m.p. 104-105° and 1:2, m.p. 61-66°). The $XeOF_4$, in the SbF_5 complexes, is certainly no longer molecular, as in the 1:1 $XeF_2 \cdot XeOF_4$ molecular adduct[12], and the marked increase in the Xe-F stretching frequency clearly evinces cation formation. Further-more, comparisons of the Raman spectra of the SbF_5 complexes, given in Figure 1, indicate the salt formulations $XeOF_3^+SbF_6^-$ and $XeOF_3^+Sb_2F_{11}^-$. The similarities of the $XeOF_3^+$ and XeF_3^+ spectra suggest a close structural relationship. It is therefore probable that the $XeOF_3^+$ geometry will be very like that of XeF_3^+ to which an oxygen atom has been added at a Xe electron-pair site (equatorial).

The similarity of the Xe-O stretching frequencies suggests that the Xe-O bonds in $XeOF_3^+$ and $XeOF_4$ must be nearly the same. Also, that the axial stretching frequencies of $XeOF_3^+$ lie somewhat higher than

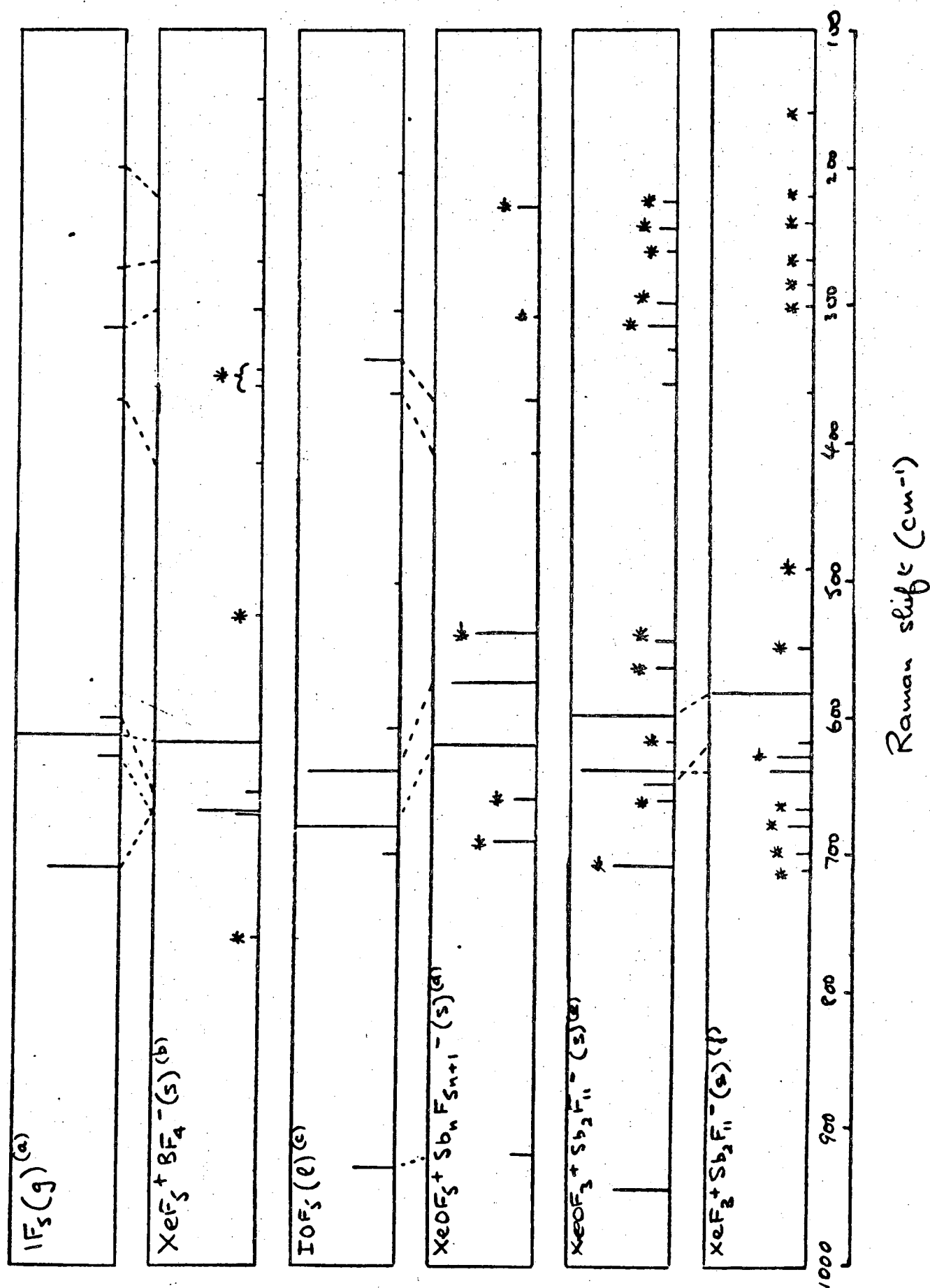those of XeF_3^+ indicates that the Xe-F axial bonds will be slightly shorter in the former than in the latter.

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Figure 1: Raman Spectra of Xenon-Cation Species and Iodine Relatives

$IF_5 (g)$ [a]

$XeF_5^+ BF_4^- (s)$ [b]

$IOF_5 (\ell)$ [c]

$XeOF_5^+ Sb_n F_{5n+1}^- (s)$ [d]

$XeOF_3^+ Sb_2 F_{11}^- (s)$ [e]

$XeF_3^+ Sb_2 F_{11}^- (s)$ [f]

Raman shift (cm^{-1})

Footnotes for Figure 1.

* Raman line assigned to anion.

(a) Ref. 14.

(b) C. J. Adams and N. Bartlett, to be published. The fundamental frequencies of XeF_5^+ are sensitive functions of the counterion and phase, although solid $XeF_5^+BF_4^-$ is a typical example. Common values for the stretching frequencies are: $\nu_1(a_1)$ 650-680 cm^{-1}; $\nu_2(a_1)$ 585-630 cm^{-1}; $\nu_4(b_1)$ 600-640 cm^{-1}; $\nu_7(e)$ 640-670 cm^{-1}.

(c) Ref. 15.

(d) This work. Lines attributable to dioxygenyl fluoroantimonates have been deleted.

(e) This work. Assignments for $XeOF_3^+$: 944 cm^{-1}, $\nu(Xe-O)$; 649, ν_{asym} (ax. XeF_2); 638, $\nu(eq. Xe-F)$; 601 ν_{symm} (ax. XeF_2); 358, 333, $\delta(FXeF)$, $\delta'(OXeF)$. Our assignments differ from those of Gillespie et al. (Ref. 9) only in placing ν_{asym} (ax. XeF_2) higher than ν_{symm} (ax. XeF_2), as has been found for structurally related molecules, e.g. TeF_4 (Ref. 16).

(f) This work. Assignments for XeF_3^+: 640 cm^{-1}, $\nu(eq. Xe-F)$; 618 ν_{asym} (ax. XeF_2); 582 ν_{symm} (ax. XeF_2); 363 $\delta(FXeF)$.

NOTE TO PRINTER: Figure 2 comprises the drawing (page 9) and the
table (page 10).
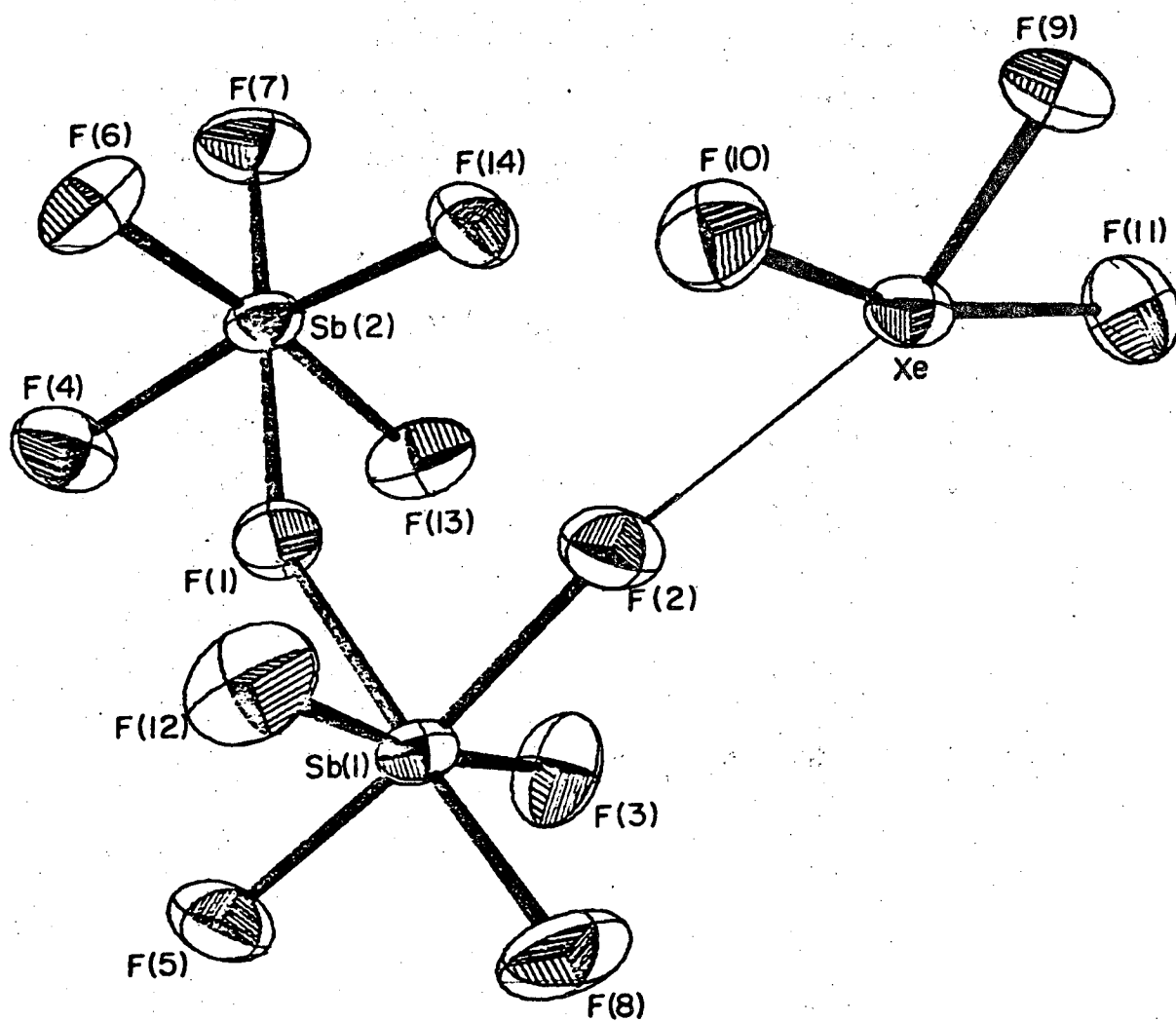
Figure 2: The $XeF_3^+Sb_2F_{11}^-$ structure unit.

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Distances (Å)		Angles (Deg.)	
Xe-Fe(2)	2.50(1)	F(9)-Xe-F(10)	81.73(30)
Xe-F(9)	1.83(1)	F(9)-Xe-F(11)	80.22(30)
Xe-F(10)	1.88(1)	F(10)-Xe-F(11)	161.90(40)
Xe-F(11)	1.89(1)	F(10)-Xe-F(2)	72.67(27)
		F(9)-Xe-F(2)	154.39(38)
Sb(1)-F(1)	2.01(1)		
Sb(1)-F(2)	1.90(1)	Xe-F(2)-Sb(1)	171.64(13)
Sb(1)-F(3)	1.85(1)	Sb(1)-F(1)-Sb(2)	155.37(15)
Sb(1)-F(5)	1.84(1)		
Sb(1)-F(8)	1.85(1)		
Sb(1)-F(12)	1.83(1)		

Figure 2: The $XeF_3^+Sb_2F_{11}^-$ Structure unit.